Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay

S.S. Tahir, Naseem Rauf *

Environmental Analytical Laboratory, Pakistan Council of Scientific & Industrial Research, Plot # 16, H-9, Islamabad, Pakistan

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Abstract

The ability of bentonite to remove malachite green from aqueous solutions has been studied for different adsorbate concentrations by varying the amount of adsorbent, temperature, pH and shaking time. Maximum adsorption of the dye, i.e. >90% has been achieved in aqueous solutions using 0.05 g of bentonite at a pH of 9. Thermodynamic parameters such as $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ were calculated from the slope and intercept of the linear plots of $\ln K_D$ against $1/T$. Analysis of adsorption results obtained at 298, 308, 318 and 328 K showed that the adsorption pattern on bentonite seems to follow the Langmuir, Freundlich and D–R isotherms. The temperature increase reduces adsorption capacity by bentonite, due to the enhancement of the desorption step in the mechanism. The numerical values of sorption free energy ($E_a$) of 1.00–1.12 kJ mol$^{-1}$ indicated physical adsorption. The kinetic data indicated an intraparticle diffusion process with sorption being first order. The rate constant $k$ was 0.526 min$^{-1}$. The concentration of malachite green oxalate was measured before and after adsorption by using UV–Vis spectrophotometer.

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Keywords: Adsorption capacity; Langmuir; Freundlich; D–R isotherm; Kinetics; Surface charge; Bentonite

1. Introduction

Malachite green oxalate has found extensive use all over the world in the fish farming industry as a fungicide, ectoparasiticide and disinfectant (Alderman, 1985). This dye has also been used extensively for dyeing silk, wool, jute, leather and cotton (Culp and Beland, 1996). It belongs to the group of triphenylmethane dyes. Malachite green is highly cytotoxic to mammalian cells and also acts as a liver tumor-enhancing agent (Rao, 1995). Due to these facts, malachite green is on the Food and Drug Administration’s (FDA’s) priority list for fish drugs that need analytical methods of development (Rushing and Hansen, 1997). In response to concerns regarding the health risks associated with the use of dyes, adsorption is, by far, the most versatile and widely used technique for the removal of dyes from aqueous solutions (Alderman, 1985; Culp and Beland, 1996).

Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon (Rao, 1995; Rushing and Hansen, 1997), peat (Allen, 1996; Ho and McKay, 1998), chitin (McKay et al., 1983; silica McKay, 1984) and others (El-Geundi, 1991; Hu, 1996; Juang et al., 1997; Low and Lee, 1997; Namasiyayam et al., 1998; Aksu, 2001; Tsai et al., 2001; Robinson et al., 2002). However, the amount (g) of dyes adsorbed on the above adsorbents...
(kg) are not very high, some have capacities between 200 and 600 g kg⁻¹ and some even lower than 50 g kg⁻¹. To improve the efficiency of the adsorption processes, it is essential to develop the more effective and cheaper adsorbents with higher adsorption capacities.

Recently, we used bentonite clay for the successful adsorption of metal ions (Rauf et al., 1999; Naseem and Tahir, 2000, 2001; Rauf et al., 2002; Rauf et al., 2003), malathion (Pradas et al., 1993) and others (Kozar et al., 1992; Olguin et al., 1997). The adsorption of malachite green oxalate on rice husk-based porous carbon (Guo et al., 2003) and on magnetic particles (Safarik et al., 1995) has already been reported in the literature.

The objective of the present study was to assess the ability of locally available bentonite for the removal of malachite green oxalate from aqueous and optimization of conditions for its adsorption. We investigated the equilibrium and kinetics of adsorption of malachite green oxalate in solutions of pH 1–9. The Langmuir, Freundlich and D–R equations were used to fit the equilibrium isotherms. The kinetics was determined quantitatively by the pseudo first-order reaction.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals used were of analytical/laboratory grade, procured either from Merck (Germany) or BDH (UK). Malachite green oxalate was purchased from Merck. Different concentrations of malachite green oxalate were prepared from a stock of 1000 mg cm⁻³ solution. Bentonite clay was provided by a local industry located in Hattar industrial estate, Pakistan.

2.2. Adsorbent

Commercial grade bentonite, grey in color, 30-mesh size, was used as an adsorbent. It was first dried, and then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried in an electric oven at 423–473 K for several hours before use in the adsorption studies. Major elements were determined by high frequency bead sampler (OYO Danki Co-Japan) X-ray fluorescence spectrometer. The surface area of the bentonite sample was measured using a BET Quantasorb Sorption System, Model No. QS-11. Bulk density and Tap density of the bentonite were measured according to the ASTM standard methods No. B329-70 and No. B527-70 respectively and true density of the bentonite was determined using a Quantasorb (Quantachrome Corporation, New York) (Qadeer et al., 1993). The measurement of the cation exchange capacity of bentonite is made by saturating the clay with Ba²⁺ and determination of the amount held at pH 7 (Peech, 1945). For surface charge determination, method adopted by Appel and Lena (2002) was used. Concentration of Na⁺ was determined by AAS and Cl⁻ by ion analyzer (Model No. Thermo Orion EA-940) from 0.01 M NaCl solutions. PZNC value for bentonite was obtained at the point of intersection of the plot of Na⁺ and Cl⁻ as a function of pH.

2.3. Batch equilibrium studies

Malachite green oxalate solutions were prepared by dissolving dye in deionized water to the required concentrations. The pH of dye solutions was adjusted by NaOH/ HNO₃ solutions. In experiments of equilibrium adsorption isotherm, the mixture of bentonite clay (containing 0.05 g dry basis of clay), dye solution (100 cm³) were shaken for 10 min using a bath to control the temperature at 298 ± 2 K. In order to measure the dye concentration, the solutions were adjusted to pH 9 and analyzed by UV–Vis spectrometer (Analytic Jena-AG) at wavelength of 618 nm corresponding to the maximum absorbance (λ_max).

The percent adsorption and distribution coefficient (K_D in cm³ g⁻¹) were computed in the usual way (Rauf et al., 1999).

3. Results and discussion

Composition of the bentonite is presented in Table 1. SiO₂ and Al₂O₃ are the major constituents of the clay with other oxides present in trace amounts, so it is expected that either any of the major oxides (SiO₂ and Al₂O₃) present in the adsorbent or their combined influence are likely to be responsible for the adsorption of dye.

The bulk, tap and true density of the bentonite clay determined were 0.83, 1.22 and 2.90 g cm⁻³. The low

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage by weight/unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>61.46</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>18.74</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.49</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.55</td>
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<tr>
<td>MnO</td>
<td>0.07</td>
</tr>
<tr>
<td>MgO</td>
<td>5.42</td>
</tr>
<tr>
<td>CaO</td>
<td>2.05</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.09</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.93</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.11</td>
</tr>
<tr>
<td>LOI</td>
<td>7.56</td>
</tr>
</tbody>
</table>

LOI: loss on ignition.
surface area (46.61 m² g⁻¹) value obtained for bentonite is interesting in view of the fine-grain and the expanding-lattice characteristics of the mineral. The low value for bentonite means that the major part of the potential surface of the mineral could not be reached by the nitrogen or other gases used in the determinations (Ralph, 1968). The cation exchange capacity of the bentonite determined is 95 meq 100 g⁻¹. With regard to exchangeable cations, Ca²⁺ is the most abundant ion. Mg²⁺ is frequently present as an exchangeable ion in relatively small amounts, and this is particularly the case when Ca²⁺ is the dominant ion (Ralph, 1968).

Although bentonite clay has an overall neutral charge, it has an excess negative charge on its lattice and is characterized by a three-layer structure with two silicate layers enveloping an aluninate layer (Ramakrishna and Viraraghavan, 1997). This arises from the partial replacement of tetravalent silica with trivalent aluminum that leads to the replacement of trivalent aluminum with divalent calcium. Since opposite charges attract, the negatively charged surface lattice of the bentonite clay may have an affinity for cationic dye. Thus, it could be assumed that bentonite clay may have a greater capacity to adsorb cationic dye. This is supported by the experimental findings (Ramakrishna and Viraraghavan, 1997), where bentonite clay exhibited high removals of a cationic Basic Blue 9 and Thioflavin T dye.

### 3.1. Adsorption isotherms

Fig. 1 shows the Langmuir adsorption isotherms of the dye at 298, 308, 318 and 328 K using the bentonite clay. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once a dye molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value is reached, beyond which no further sorption can take place. Compared to the Langmuir isotherm, the Freundlich model is generally found to be better suited for characterizing multi-layer adsorption processes. The Langmuir parameters, Q₀ and b were computed from the slopes and intercepts of the straight lines of plots of (C / qₑ) vs. Cₑ (Fig. 1), while the values of Freundlich constants, i.e. k and 1/n were calculated from the plots (Fig. 2) of log Cₑ against log X/m (Namasivayam and Ranganthan, 1993). Q₀ and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively, while k indicates the adsorption capacity and 1/n is indicative of the intensity of reaction. Parameters of the Langmuir and Freundlich isotherms are computed in Table 2. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L (Namasivayam and Ranganthan, 1993), which is defined by

\[
R_L = 1/(1 + bC_0)
\]

where b is Langmuir constant and C₀ is the initial concentration of the dye. The value of R_L calculated from the above expression (Eq. (1)), lies in the range of 0.962–0.999, indicates favorable adsorption of malachite green oxalate on bentonite for all studied concentrations at 298, 308, 318 and 328 K.

The adsorption data was also tested for the Dubinin–Radushkevich (D–R) isotherm equation (Dubinin and Radushkevich, 1947).

The D–R plots (Fig. 3) of ln X/m against \( \varepsilon^2 \) indicates a straight line with a regression coefficient (r) of >0.990. The values of \( k' \) and \( X'm \) evaluated from the slopes and intercepts of these plots are given in Table 2.

From the \( k' \) values the mean energy of adsorption, \( E_a \) can be calculated using the relation (Hobson, 1969).

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**Fig. 1.** Langmuir plots for the adsorption of malachite green oxalate on to bentonite at different temperatures where (○) 298 K; (□) 308 K; (△) 318 K; (◇) 328 K. Experimental conditions: amount of bentonite = 0.05 g; shaking time = 10 min; aqueous medium.

**Fig. 2.** Freundlich plots for the adsorption of malachite green oxalate on to bentonite at different temperatures where (○) 298 K; (□) 303 K; (△) 318 K; (◇) 328 K. Experimental conditions: amount of bentonite = 0.05 g; shaking time = 10 min; aqueous medium.
The mean energy of adsorption is the free energy change when one mole of the ion is transferred to the surface of the solid from infinity in the solution. Its value in the range of 1–8 kJ mol\(^{-1}\) indicates physical adsorption, while its value in the range of 20–40 kJ mol\(^{-1}\) is indicative of the chemisorption (Helferrich, 1962; Rieman and Walton, 1970). The values of \(E_a\) in the present case (Table 2) were determined at different temperatures and found to lie between 1.00 and 1.13 corresponding to physical adsorption.

### 3.2. Kinetic studies

The time dependent dye adsorption behavior was measured by varying the equilibrium time between adsorbate and adsorbent in the range of 1–60 min. The percentage adsorption of the dye as a function of contact time plotted in Fig. 4 indicates that the equilibrium between the dye and the bentonite was attained within 10 min. Three consecutive steps are involved in the removal of dye from water on bentonite. First, the adsorbate species migrate from the bulk liquid phase to the outer surface of adsorbent particles (film diffusion). Secondly, the dye species move within the micro- and macro-pores of adsorbent particles (pore diffusion). Thirdly, the reaction of adsorbate–adsorbent species takes place on the surface.

The kinetics of the dye adsorption on bentonite follows the first-order rate expression given by (Lagergren, 1898).

\[
\ln \frac{q}{q_e} = \frac{-t}{K_{ad} t}
\]

The linearity of the plot of \(\log(q_e - q)\) versus \(t\) (Fig. 5) indicates the applicability of the first-order rate expression. The \(K_{ad}\) value, calculated from the slope of the line in Fig. 5 is 0.526 min\(^{-1}\).

### 3.3. Effect of pH

The influence of pH on the dye adsorption onto bentonite was studied while the dye concentration, shaking time and amount of bentonite were fixed at 56.8 mg cm\(^{-3}\), 10 min and 0.05 g respectively. The variation of malachite green adsorption on bentonite over a pH range of 2.0–10.0 is shown in Fig. 6. The result reveals that the adsorption of the dye increases from

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**Table 2**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
</tr>
<tr>
<td><strong>Langmuir isotherm</strong></td>
<td></td>
</tr>
<tr>
<td>(Q_0) (mg g(^{-1}))</td>
<td>7.716</td>
</tr>
<tr>
<td>(b) (l mg(^{-1}) g(^{-1}))</td>
<td>0.0386</td>
</tr>
<tr>
<td><strong>Freundlich isotherm</strong></td>
<td></td>
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<tr>
<td>(n)</td>
<td>1.38</td>
</tr>
<tr>
<td>(K) (mg(^{1-n}) l(^n) g(^{-1}))</td>
<td>1.72 \times 10(^{-3})</td>
</tr>
<tr>
<td><strong>D–R isotherm</strong></td>
<td></td>
</tr>
<tr>
<td>(X_m) (mg g(^{-1}))</td>
<td>4.53 \times 10(^{-4})</td>
</tr>
<tr>
<td>(K) (mol(^2) kJ(^{-2}))</td>
<td>0.529</td>
</tr>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>1.000</td>
</tr>
</tbody>
</table>

---

**Fig. 3.** D–R Plot for the adsorption of malachite green oxalate onto bentonite at different temperatures where (○) 298 K; (□) 308 K; (△) 318 K; (apg) 328 K.

\[
E_a = (-2K)^{-1/2}
\]
29% to 91% with an increase in pH of the solution from 2.0 to 9.0 and then remains almost constant. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH. The pH PZC value for bentonite was 2.2 (Fig. 6). At pH values below PZC, the clay had net positive charge and would, therefore, be prone to electrostatically repel cations. Malachite green is a cationic basic dye as denoted by the presence of the positive nitrogen ion in its structure. On dissolution, the oxalate ion enters the aqueous solution ensuring that the dye has an overall positive charge. The positive charge on the cationic dye should ensure that it is attracted by an anionic adsorbent.

In clay-aqueous systems the potential of the surface is determined by the activity of ions (e.g., H⁺ or pH), which react with the mineral surface. For clay minerals the potential determining ions are H⁺ and OH⁻ and complex ions formed by bonding with H⁺ and OH⁻. The broken Si–O bonds and Al–OH bonds along the surfaces of the clay crystals result in hydrolysis.

At low pH the reaction might be:

\[
\text{SiOH} + \text{H}^+ \rightarrow \text{SiOH}_2^+
\]

At high pH the reaction is:

\[
\text{SiOH} + \text{OH}^- \rightarrow \text{SiO}^- + \text{H}_2\text{O}
\]

In our studies the adsorption is maximum at pH 9. So at high pH, the solution in contact with the basal oxygen surface of the tetrahedral sheet will contain excess hydroxyls. The surface will then exhibit a cation exchange capacity.

3.4. Thermodynamic studies

The influence of temperature on the dye adsorption was investigated over the concentration ranges of 50 g cm⁻³, 70 g cm⁻³, 90 g cm⁻³, 140 g cm⁻³ at 298, 308, 318 and 328 K under the optimized conditions of 10 min of shaking time, 0.05 g of adsorbent, and a pH of 5.6. Fig. 7 shows the Van’t Hoff plots of ln \( K_D \) versus

![Van't Hoff plots](image)

Fig. 7. The van’t Hoff plots for the adsorption of malachite green oxalate onto bentonite where (△) 50 mg cm⁻³; (□) 70 mg cm⁻³; (▲) 90 mg cm⁻³; (○) 140 mg cm⁻³.

<table>
<thead>
<tr>
<th>Concentration of malachite green oxalate (mg cm⁻³)</th>
<th>Δ( H^\circ ) (kJ mol⁻¹)</th>
<th>Δ( S^\circ ) (kJ mol⁻¹ K⁻¹)</th>
<th>−Δ( G^\circ ) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>308 K</td>
<td>318 K</td>
<td>328 K</td>
</tr>
<tr>
<td>50</td>
<td>0.0134</td>
<td>0.0336</td>
<td>11.0054</td>
</tr>
<tr>
<td>70</td>
<td>0.0206</td>
<td>0.0088</td>
<td>2.8952</td>
</tr>
<tr>
<td>90</td>
<td>0.0210</td>
<td>0.0065</td>
<td>2.1053</td>
</tr>
<tr>
<td>140</td>
<td>0.0295</td>
<td>0.0243</td>
<td>8.0095</td>
</tr>
</tbody>
</table>

Table 3
Thermodynamic parameters for the adsorption of malachite green on to bentonite

![Effect of pH on the adsorption of malachite green oxalate on to bentonite and the relationship between the net negative/positive surface charge of the clay and pH of the solution](image)

Fig. 6. Effect of pH on the adsorption of malachite green oxalate on to bentonite and the relationship between the net negative/positive surface charge of the clay and pH of the solution (\( I = 0.01 \) M NaCl).
1/T. The values of $\Delta H^\circ$ and $\Delta S^\circ$ and $\Delta G^\circ$ were calculated as previously (Naseem and Tahir, 2000). Positive values of $\Delta H^\circ$ and $\Delta S^\circ$ suggest endothermic reaction, while the negative values of free energy change ($\Delta G^\circ$) indicate that the adsorption is spontaneous (Table 3). The positive values of $\Delta S^\circ$ suggest the increased randomness at the solid–solution interface during desorption of malachite green oxalate on bentonite. In desorption of the dye, the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system (Namasivayam and Ranganthan, 1993).

4. Conclusions

Bentonite deposits have been reported in different parts of the country. In the present study, bentonite clay was selected as a local, cheaper and readily available adsorbent for the removal of Malachite green oxalate from the aqueous solutions. Adsorption of the dye was studied by batch technique and it was observed that >90% of dye removal was achieved by using 0.05 g of bentonite. The kinetics of adsorption developed can be used to achieve low levels of dye from aqueous solutions utilizing bentonite. Almost 91% removal of dye was observed at pH of 9. The adsorption data seems to follow the Langmuir, Freundlich and D–R adsorption isotherms.

References


Namasivayam, C., Ranganthan, K., 1993. Waste Fe(III)/Cr(III) sludge as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewa-


